

Claims:

- 1        The method of carboxylating wood pulp in a wood pulp bleach plant by adding a base chemical to the pulp slurry after a bleach stage washer, adding catalytic oxidation chemicals to the pulp slurry and reacting the chemicals with the pulp between  
5        the bleach stage washer and the next bleach stage to form oxidized pulp, adding stabilizing chemicals to the catalytically oxidized pulp before the next bleach stage, and stabilizing the catalytically oxidized pulp in the next bleach stage.
- 2        The method of Claim 1 in which said bleach stage is an extraction stage.
- 3        The method of Claim 1 in which said bleach stage is a chlorine dioxide  
10       stage.
- 4        The method of Claim 1 in which the base chemical is sodium hydroxide or sodium carbonate.
- 5        The method of Claim 1 in which the oxidizing chemicals are a sufficient amount of a primary oxidant selected from the group consisting of hindered heterocyclic  
15       oxammonium salts in which the carbon atoms adjacent the oxammonium nitrogen lack .alpha.-hydrogen substitution, the corresponding amines, hydroxylamines, and nitroxides of these oxammonium salts, and mixtures thereof, and a secondary oxidant selected from chlorine dioxide and latent sources of chlorine dioxide in a sufficient amount to induce an increase in carboxyl substitution in the carbohydrate of at least 2 meq/100 g.
- 20       6        The method of Claim 5 in which the nitroxides have a five or six membered ring structure with di-lower alkyl substitution on each carbon atom adjacent the nitroxide.
- 7        The method of Claim 4 in which the nitroxides are compositions having the structure in which R<sub>1</sub>- R<sub>4</sub> are one to four carbon alkyl groups but R<sub>1</sub> with R<sub>2</sub> and R<sub>3</sub>  
25       with R<sub>4</sub> may together be included in a five or six carbon alicyclic ring structure, X is sulfur or oxygen, and R<sub>5</sub> is hydrogen, C<sub>1</sub>- C<sub>12</sub> alkyl, benzyl, 2-dioxanyl, a dialkyl ether, an alkyl polyether, or a hydroxyalkyl, and X with R<sub>5</sub> being absent may be hydrogen or a mirror image moiety to form a bipiperidinyl nitroxide.
- 8        The method of Claim 5 in which the nitroxides are compositions having  
30       the structure in which R<sub>1</sub>- R<sub>4</sub> are one to four carbon alkyl groups but R<sub>1</sub> with R<sub>2</sub> and R<sub>3</sub> with R<sub>4</sub> may together be included in a five or six carbon alicyclic ring structure, and R<sub>6</sub> is hydrogen or C<sub>1</sub>- C<sub>5</sub> alkyl, and R<sub>7</sub> is hydrogen, C<sub>1</sub>- C<sub>8</sub> alkyl, phenyl, carbamoyl, alkyl carbamoyl, phenyl carbamoyl, or C<sub>1</sub>- C<sub>8</sub> acyl.

- 9        The method of Claim 5 in which the nitroxides are compositions having the structure in which R<sub>1</sub>- R<sub>4</sub> are one to four carbon alkyl groups but R<sub>1</sub> with R<sub>2</sub> and R<sub>3</sub> with R<sub>4</sub> may together be included in a five or six carbon alicyclic ring structure, and X is oxygen, sulfur, NH, N-alkyl, NOH, or NOR<sub>8</sub> where R<sub>8</sub> is lower alkyl.
- 5            10        The method of Claim 5 in which the nitroxides are compositions having the structure wherein R<sub>1</sub>- R<sub>4</sub> are one to four carbon alkyl groups but R<sub>1</sub> with R<sub>2</sub> and R<sub>3</sub> with R<sub>4</sub> may together be included in a five or six carbon alicyclic ring structure, X is methylene, oxygen, sulfur, or alkylamino, and R<sub>9</sub> and R<sub>10</sub> are one to five carbon alkyl groups and may together be included in a five or six member ring structure which, in turn,
- 10        may have one to four lower alkyl or hydroxy alkyl substituents.
- 11        The method of Claim 10 in which the primary oxidant is EGK-TAA.
- 12        The method of Claim 1 in which the stabilizing compound is selected from the group consisting of alkali metal chlorites, chlorine dioxide, hydrogen peroxide, acid, peracids, and mixtures thereof.
- 15            13        The method of Claim 1 in which the stabilizing chemical is an acid.
- 14        The method of Claim 13 in which the stabilizing chemical further comprises a peroxide.
- 15        The method of Claim 14 in which the stabilizing chemical further comprises chlorine dioxide.
- 20            16        The method of Claim 1 in which said carboxylation reaction has a reaction time of no more than 15 minutes.
- 17        The method of Claim 1 in which said carboxylation reaction has a reaction time of no more than 2 minutes.
- 18        The method of Claim 1 in which said carboxylation reaction has a reaction
- 25        time of no more than 1 minute.
- 19        The method of Claim 1 in which said carboxylation reaction has a reaction time of no more than 30 seconds.
- 20        The method of Claim 1 in which said carboxylation reaction has a reaction time of no more than 15 seconds.